



# Fluorinated polymers based on pyrazole groups for fuel cell membranes

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## ABSTRACT

The synthesis and characterization of two fluorinated copolymers bearing pyrazole group as precursor of proton-conducting membranes in polymer electrolyte fuel cells are described. 1-Benzyl-5-methyl-3-hydroxymethyl-pyrazole was first synthesized in a two step-reaction. It was then grafted onto poly(chlorotrifluoroethylene -*alt*-2-iodoethyl vinyl ether) copolymer (poly(CTFE-*alt*-IEVE)). The degree of grafting was controlled by the reaction time, and reached 30 and 55% after 24 and 48 h, respectively. Deprotection of the benzyl group produced poly(CTFE-*alt*-IEVE)-*dep*-pyrazole<sub>y%</sub> copolymers. NMR spectroscopy enabled to monitor all reaction steps and ensured the purity of these functional fluorinated copolymers. The poly(CTFE-*alt*-IEVE)-*dep*-pyrazole<sub>y%</sub> copolymers were thermally stable (up to 200 °C under air) and showed a maximum proton conductivity of  $4 \times 10^{-5}$  mS cm<sup>-1</sup> at 180 °C under anhydrous conditions. From cyclic voltammetry (CV), these copolymers displayed an electrochemical stability domain extended over 2.0 V.

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## 1. Introduction

Proton exchange membranes for fuel cell (PEMFC) are characterized by the high energetic performance, low noise emissions, and can operate without generating hazardous and polluting products [1,2]. PEMFCs need a membrane to split the chemical reactions at the anode from the cathode both chemically and electronically [3–6]. For the good operation of the cell, this membrane must present efficient proton transfer, an impermeability towards dihydrogen and dioxygen, a thermal stability, chemical resistance and good mechanical properties. At present, the most extensively utilized polymer electrolyte membrane are Nafion<sup>®</sup>, Aquavion<sup>®</sup>, 3M<sup>®</sup>, Flemion<sup>®</sup>, Fumion<sup>®</sup> membranes, that exhibit high proton conductivity and chemical stabilities [7,8]. However, these membranes have three major disadvantages: (i) their high price, (ii) a loss of electrochemical performances from 80 °C, and (iii) their methanol crossover. To overcome these limitations, Kreuer [9] proposed the substitution of water as proton carrier by solvent immobilization brought by N-heterocycles, such as imidazole, benzimidazole, and tetrazole.

To the best of our knowledge, pyrazolic compounds seem attractive and these derivatives have been used in different areas, such as pharmacology [10], biology [11], catalysis [12], and electronics [13]. Therefore, it was worth attempting to synthesize copolymers that bear pyrazolic moieties in the aim to develop a new generation of high temperature-membranes for fuel cell. In fact, fluorinated copolymers [14–16] exhibit remarkable properties such as chemical, thermal,

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oxidative and electrical stability, low dielectric constants, and low inflammability. For these reasons, they are involved as high value added materials and devices for high tech-application such as optics, aerospace, cars, lithography, coatings and energy [17,18]. Nevertheless, the synthesis of a fluorinated polymer containing pyrazole groups has not been reported yet in the literature. Hence, the aim of this article deals with the design of original fluorinated copolymers bearing pyrazolic dangling groups from the synthesis of new pyrazolic compounds and their grafting onto an alternating fluorinated copolymer. The thermal and electrochemical properties of these resulting copolymers are then examined and compared.

## 2. Experimental

### 2.1. Materials

*Tert*-butyl peroxyphthalate (TBPPI, Trigonox 25- C75, 75 wt% solution in isododecane) was kindly provided by Akzo Nobel (Compiègne, France). Chlorotrifluoroethylene (CTFE) was supplied by Honeywell S.A. 1,1,1,3,3-Pentafluorobutane (C<sub>4</sub>F<sub>5</sub>H<sub>5</sub>) (97%) was kindly provided by Solvay S.A. (Brussels, Belgium) and distilled prior to use. 2-Chloroethyl vinyl ether (CEVE) (99%), sodium iodide (NaI) (99.99%), potassium *tert*-butyl hydroxide (tBuOK) (98%), sodium hydroxide (NaOH) (97%), acetone, dimethyl sulfoxide, methanol, diethyl ether, dichloromethane, were purchased from Sigma–Aldrich. Deuterated solvents for NMR were purchased from Euriso-top (Grenoble, France) (purity > 99.8%).

All reagents were used without further purification except for 1,1,1,3,3-pentafluorobutane and acetone, which were distilled prior to use.

### 2.2. Characterization

NMR spectra were recorded on a Bruker AC 400 or 250 instrument, using deuterated dimethyl sulfoxide or chloroform as the solvent and tetramethylsilane (TMS) as the references for <sup>1</sup>H, <sup>19</sup>F or <sup>13</sup>C nuclei. In the figures and discussion below, the letters s, d, t, q, and m stand for singlet, doublet, triplet, quintet, and multiplet, respectively. Chemical shifts are given in ppm.

Mass spectra were determined on a Platform II Micromass instrument (ESI<sup>+</sup>, CH<sub>3</sub>CN/H<sub>2</sub>O: 50/50).

Uncorrected Melting Points (T<sub>m</sub>) were determined in capillary on IA9100 (Electrothermal) apparatus.

Gel permeation chromatography (GPC) or size exclusion chromatography (SEC) was achieved by means of a Spectra Physics Winner Station, a Waters Associate R 401 differential refractometer, and a set of four columns connected in series: Styragel (Waters) HR4 5 μm, HR3 analyses 5 μm, PL and Gel (Polymer Laboratories), 5 μm and 100 Å. Monodispersed poly (methyl methacrylate), PMMA standards, were used for calibration. Aliquots were sampled from the reaction medium, diluted with dimethylformamide (DMF) up to a known concentration (C<sub>p</sub>, t) ~ 2% wt%, filtered through a 20 μm out PTFE Chromafil membrane, and finally analyzed by GPC at 30 °C, at a flow rate of 0.8 mL/min.

Thermogravimetric analyses (TGA) were performed in air with a Q50 apparatus from TA Instruments at a heating rate of 10 °C min<sup>-1</sup> from room temperature up to 800 °C. The sample size varied between 10 and 15 mg.

Differential scanning calorimetry (DSC) measurements on copolymers were recorded at a heating rate of 20 °C min<sup>-1</sup> from -100 to +200 °C, and a cooling rate of 20 °C min<sup>-1</sup>. A second scan was required for the assessment of the glass transition temperature, T<sub>g</sub>, determined at the inflection point in the heat capacity jump. The sample size was about 10 mg.

Cyclic voltammograms (CV) were obtained with voltalab PGZ 100. Voltammograms of all polymers were recorded in a three-electrode CV system (Fig. S16), using a polymer electrolyte modified Pt working electrode and a Pt counter electrode. The reference electrode was silver/silver chloride (Ag/AgCl) calibrated by a ferrocene/ferricinium redox system. Cyclic voltammetry studies were carried out in 0.1 M tetraethylammonium tetrafluoroborate (TEATFB)/acetonitrile.

The proton conductivity of the copolymer samples were determined with the electrical assembly (represented in Fig. S1 of the Supporting Information), in the frequency range from 10<sup>0</sup> to 10<sup>7</sup> Hz for each temperature and under a flow of dry nitrogen (0% RH). Hot pressed pellets (compressed at 1.27 × 10<sup>3</sup> MPa) from dried and grinded poly(CTFE-*alt*-IEVE)-*dep*-pyrazole<sub>y%</sub> copolymers were placed between platinum plates and their conductivities were measured *versus* temperature (80–180 °C). Prior to conductivity measurements, the samples were dried under vacuum at 70 °C for 2 days to minimize the content of moisture. The conductivity (σ) was calculated by the following equation:

$$\sigma_{AC} = \frac{I \cdot L}{U \cdot S} = \frac{1}{R \cdot S}$$

where L, S, and R stand for the sample thickness, the cross-sectional area between pellet and electrode, and the resistance calculated from the current I and electrical voltage V (fixed at 0.5 V), respectively.

The plateau values in the medium frequency range match quite well with the σ<sub>dc</sub> obtained from the Z' minimum in the plot of imaginary part *versus* real part of the impedance (Z''/Z'), so that σ<sub>dc</sub> values could be taken from the extrapolation of the AC conductivity plateaus [19].

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